ISOLATION AND DETERMINATION OF METHYLCYCLO-PENTANE IN A MIDCONTINENT PETROLEUM [1] [2]

By Mildred M. Hicks-Bruun and Johannes H. Bruun [3]

ABSTRACT

This paper describes the isolation of methylcyclopentane from an Oklahoma petroleum. The petroleum was first fractionated by distillation into a series of 1° cuts. The fractions boiling between 68° and 78° C. were subjected to nitrating treatments in order to remove the benzene, which was previously found to be in these fractions as a constant boiling mixture with the hexane. The benzene-free fractions were then subjected to further distillations, after which the methylcyclopentane was isolated by a combination of equilibrium melting with distillation after admixture with methyl alcohol.

The following physical constants were determined for the isolated hydrocarbon: Normal boiling point, 71.8° C.; freezing point, −141.9° to −142.3° C.; specific gravity, 20°/4°, 0.7487; refractive index n_D^{20}, 1.4098; critical solution temperature with aniline, 34.7° C. The infra-red absorption spectrum was also determined.

The binary eutectic mixture of methylcyclopentane and n-hexane was found to contain 95.9 mole per cent of methylcyclopentane and to melt at −143.5° C.

The latent heat of fusion of methylcyclopentane was calculated to be 7.6 calories per gram.

From the freezing behavior the purity of the isolated sample of methylcyclopentane was found to be 98.7±0.2 mole per cent.
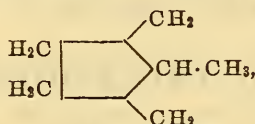
The largest amount of methylcyclopentane was in the fraction boiling between 71° and 72° C. This fraction consisted of about 82 weight per cent of methylcyclopentane. Based upon the crude petroleum the amount (4.5 kg) of the methylcyclopentane present was found to be about 0.2 of 1 per cent.

CONTENTS

I. INTRODUCTION

Although methylcyclopentane,

is one of the lowest boiling of the so-called naphthene hydrocarbons, no one has reported its isolation from petroleum in a demonstrably

pure condition. One of the probable reasons for this is the fact that its boiling point (about 72° C.) is near that of *n*-hexane (69° C.), which usually predominates in this fraction. Furthermore, the methylcyclopentane molecule has a tertiary carbon atom and a consequently great reactivity toward chemical agents. Attempts to isolate this hydrocarbon from its mixture with hexane and other compounds by means of chemical reagents, such as strong sulphuric acid, chlorosulphonic acid, fuming nitric acid, and chlorine, have failed, because the methylcyclopentane would be attacked at the same rate or even more vigorously than are the other constituents.

However, the presence of methylcyclopentane in petroleum has been indicated by different investigators. By treating a Caucasian petroleum fraction (boiling point about 70° C.) with dilute nitric acid, Markownikoff (1) [4] was able to produce small quantities of a tertiary nitroproduct which he identified with the corresponding one obtained from synthetic methylcyclopentane. Mabery and Sieplein (2) chlorinated a California petroleum fraction and found a chloride which they identified as tertiary methylpentamethylenechloride. Aschan (3) oxidized a Caucasian petroleum fraction and found succinic acid as one of the products of the oxidation. From this he concluded that methylcyclopentane was present in the petroleum.

Other investigators—for instance, Young (4)—found that the fractions of a Pennsylvania petroleum distilling around the boiling point of methylcyclopentane exhibited a high specific gravity and reacted vigorously with fuming nitric acid. Chavanne (5) in his work on a Borneo petroleum found that by plotting the weights as well as specific gravities of the fractions against their boiling ranges the maxima of these curves were exhibited by the fractions distilling around the boiling point of methylcyclopentane. By plotting the critical solution temperatures of the fractions with aniline against their boiling ranges a minimum was observed at the boiling point of methylcyclopentane.

II. METHODS EMPLOYED

The isolation of methylcyclopentane from petroleum was accomplished by means of methods and apparatus which have been described in previous papers. The following of these methods were used:

(1) Fractional distillation (6).
(2) Nitration (for removal of the benzene) (7).
(3) Equilibrium melting (7, 8).
(4) Distillation with methylalcohol (9).

III. EXPERIMENTAL PROCEDURE AND RESULTS

The present investigation deals with some of the fractions which were obtained as a result of six successive distillations of 600 gallons of an Oklahoma petroleum (10).[5] The distribution of these fractions over their boiling ranges is shown by the graph in Figure 1.[6] From

this graph it will be noted that about 6,600 g of material distilled between 70° and 73° C. The boiling point of methylcyclopentane is about 72° C.

All of the fractions were subjected to a nitrating treatment (7), in order to remove quantitatively the benzene which was present as
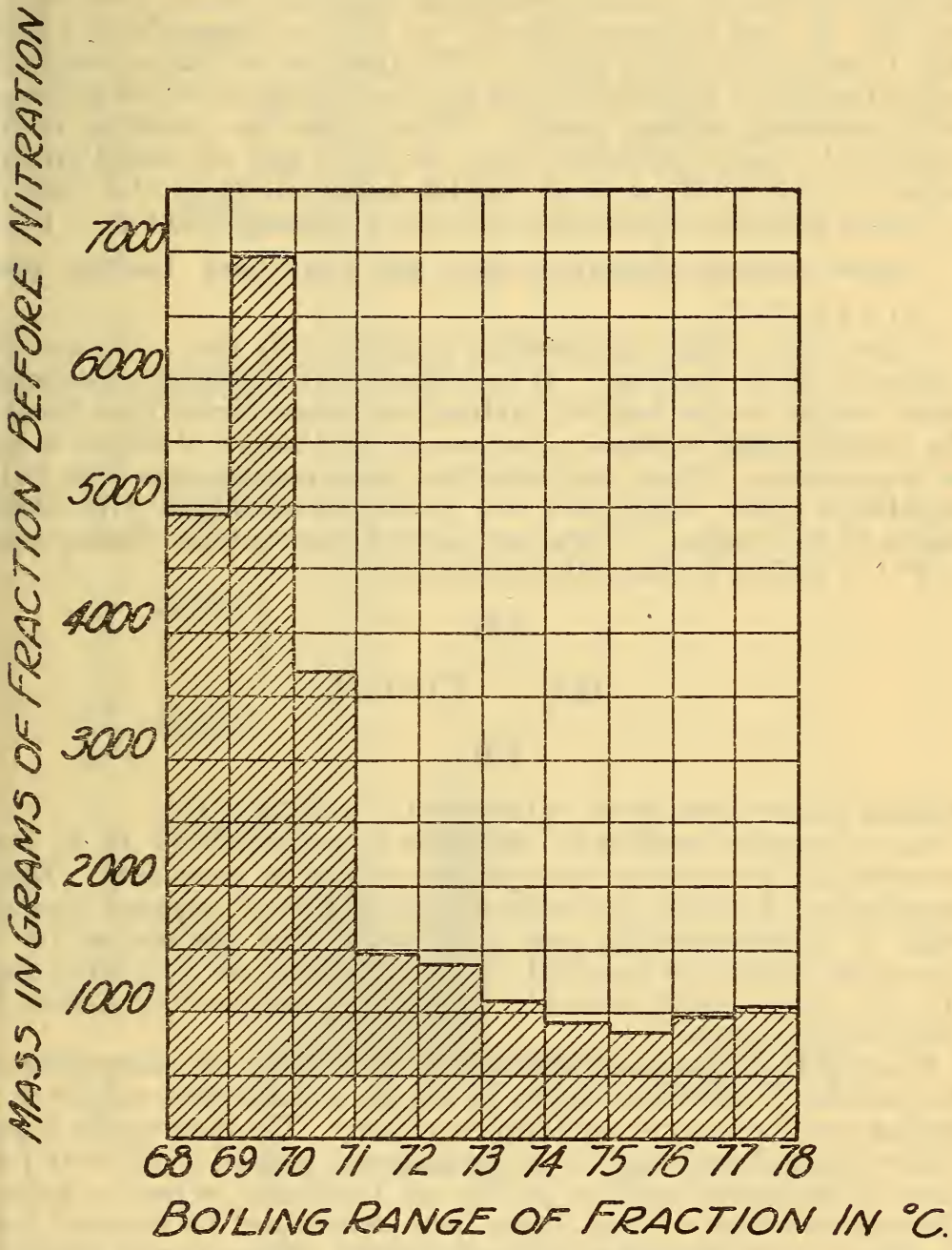
FIGURE 1.—*Distribution of the fractions over the boiling range before the removal of the benzene*

Ordinate: Mass in grams of fraction. Abscissa: Boiling range of fraction

a constant boiling mixture with the hexanes (7, 9). The benzene-free fractions were subsequently distilled four times. All of the distillations were made by S. T. Schicktanz and a staff of still operators. The boiling points of the distillates were accurately determined by means of a continuous boiling-point apparatus (7). Fractions with nearly

the same boiling points and refractive indices were mixed for further separation. After the last four distillations the fractions were redistributed, as shown by the graph in Figure 2.

By comparing Figures 1 and 2 it will be noted that the 3,700 g of material in Figure 1, with a boiling range of 70° to 71° C., by further distillation yielded additional material boiling between 69° and 70° C. and increased the 71° to 72° cut from about 1,500 g (fig. 1) to about 2,800 g (fig. 2). The fractions of this cut exhibited refractive indices which increased and freezing points which decreased with increasing boiling points. Thus while the material boiling around 71° had a refractive index of 1.394 and an initial freezing point of −111.6° C., a small fraction boiling between 71.7° and 72° C. had a refractive index of 1.405 and a freezing point of −134.3° C. (pure methylcyclopentane has: n_D^{20} 1.410 and freezing point −141.0 ± 0.3° C.).

It has been shown in previous papers (7, 9) that *n*-hexane was present in these fractions. It is evident that the other constituents must include compounds with refractive indices higher than those of the paraffin hydrocarbons. Because of the absence of olefins as well as of aromatics, it was concluded that these constituents were of the naphthene type. There are two possible naphthenes with boiling points in this region. These are methylcyclopentane (boiling point 71.9° C.) and its isomer, ethylcyclobutane,

$$
\begin{array}{ccc}
& CH_2 & \\
\diagup & & \diagdown \\
H_2C & & CH \cdot C_2H_5 \\
\diagdown & & \diagup \\
& CH_2 &
\end{array}
$$
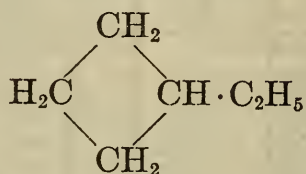
(boiling point values given between 70.5° and 72.5° C.).

As previously mentioned, different investigators (1 to 5) have reported the presence of methylcyclopentane in petroleum. Ethylcyclobutane, however, has apparently never been prepared synthetically in a demonstrably pure condition. The few values for its properties which are recorded in the literature are very discordant (11, 12) and indistinguishable from the corresponding values for methylcyclopentane.

In order to obtain more information concerning the composition of the petroleum distillates shown in Figure 2, they were subjected to further fractionation by equilibrium melting. The diagram in Figure 3 shows how the mixture (1 on the diagram) yielded in this way fractions of decreasing melting points and increasing refractive indices. Time-temperature cooling curves were determined for some of these fractions as the refractive indices increased. These curves showed a progressive decrease in initial freezing point with increasing refractive index and the same constant eutectic break (2 in fig. 3) at −143.5° C. Fractionation by equilibrium melting was no longer effective when the refractive index of the fraction reached 1.4075. The fractions with this refractive index had narrow freezing ranges, all starting at −143.5° C., and were judged to be of eutectic composition. In order to obtain further separation, the eutectic mixture (2 in fig. 3) was subjected to distillation with the addition of methyl alcohol (9).
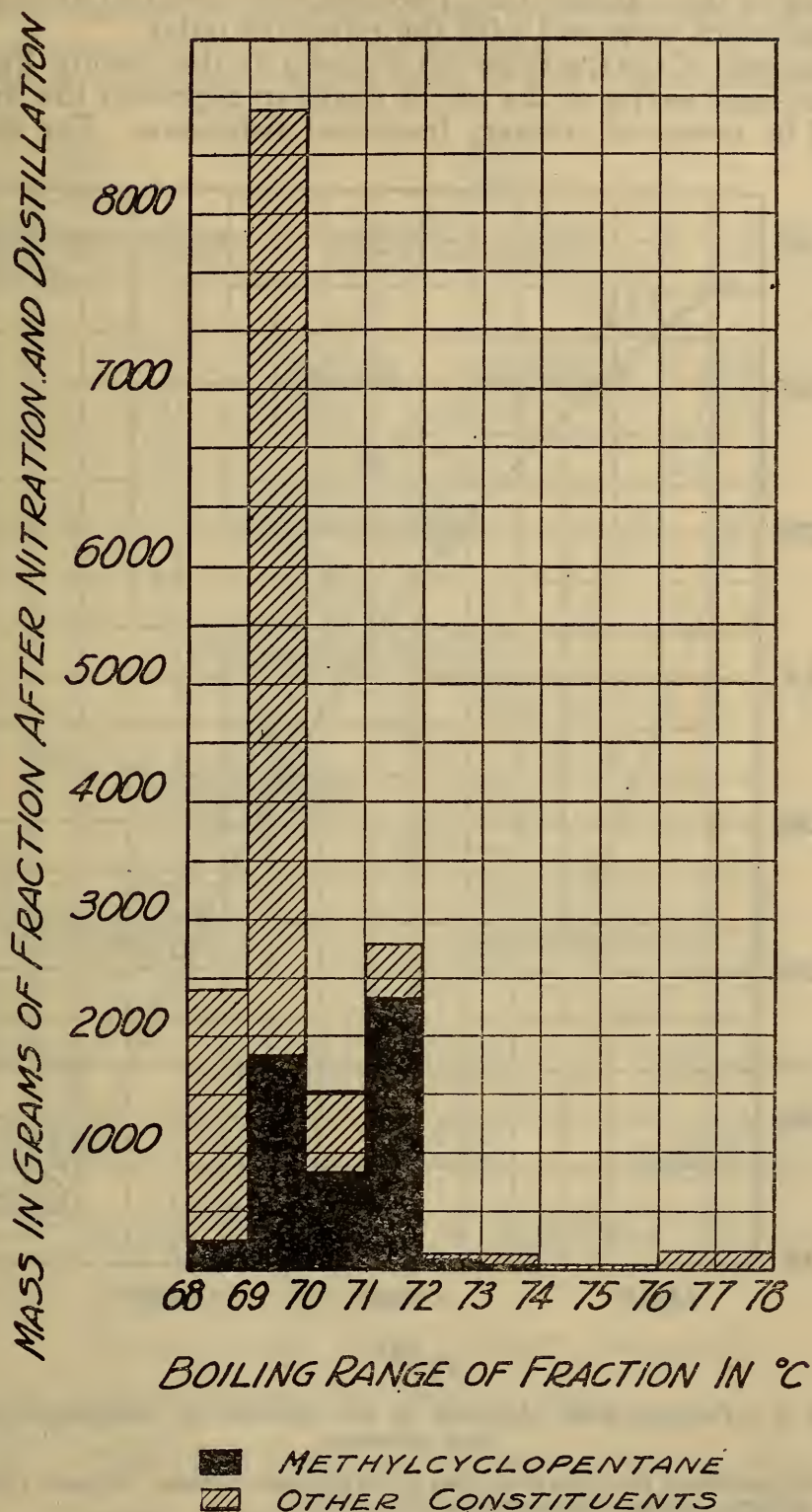
FIGURE 2.—*Distribution of the fractions over the boiling range after removal of the benzene and subsequent distillations*

The black portion of the graph indicates the amount of methylcyclopentane in the fractions. Ordinate: Mass in grams. Abscissa: Boiling range of fraction

As a result of these distillations, fractions were obtained having freezing points which increased with the refractive index.

The progress of the fractionation is shown by the chart in Figure 4. The three large circles at the top of the chart represent the fractions obtained by means of ordinary fractional distillation. The numbers
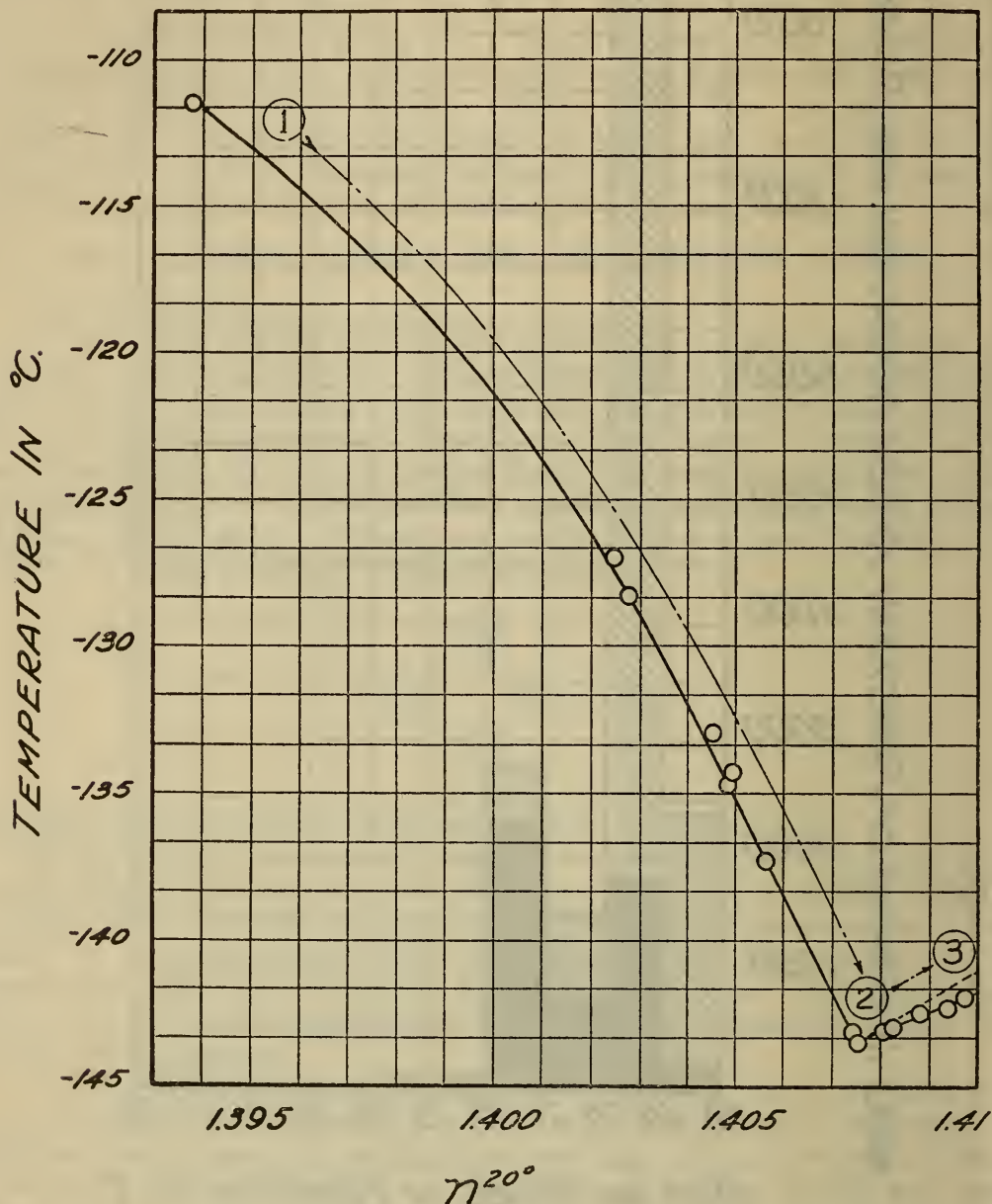
FIGURE 3.—*Freezing-point diagram of the mixtures of methylcyclopentane and n-hexane*

The small circles indicate the values determined for the petroleum fractions. Ordinate: Inital freezing point of the mixture. Abscissa: Refractive index of the mixture.

inside of the circles indicate the refractive indices of the respective fractions. The broken lines denote fractions obtained by equilibrium melting. The continuous lines show the manner in which the fractions were mixed and the dot-dash lines indicate fractionation by distillation in a 30-plate column still with the addition of methyl alcohol. The

final fractionation, indicated by crossed lines at the bottom of the chart, was made by ordinary distillation in a 60-plate column still (13).

As a result of interlocking these methods of separation, three groups of fractions with fairly constant freezing points were obtained:

Figure 4.—*Chart showing the progress of the fractionation*

Legend:
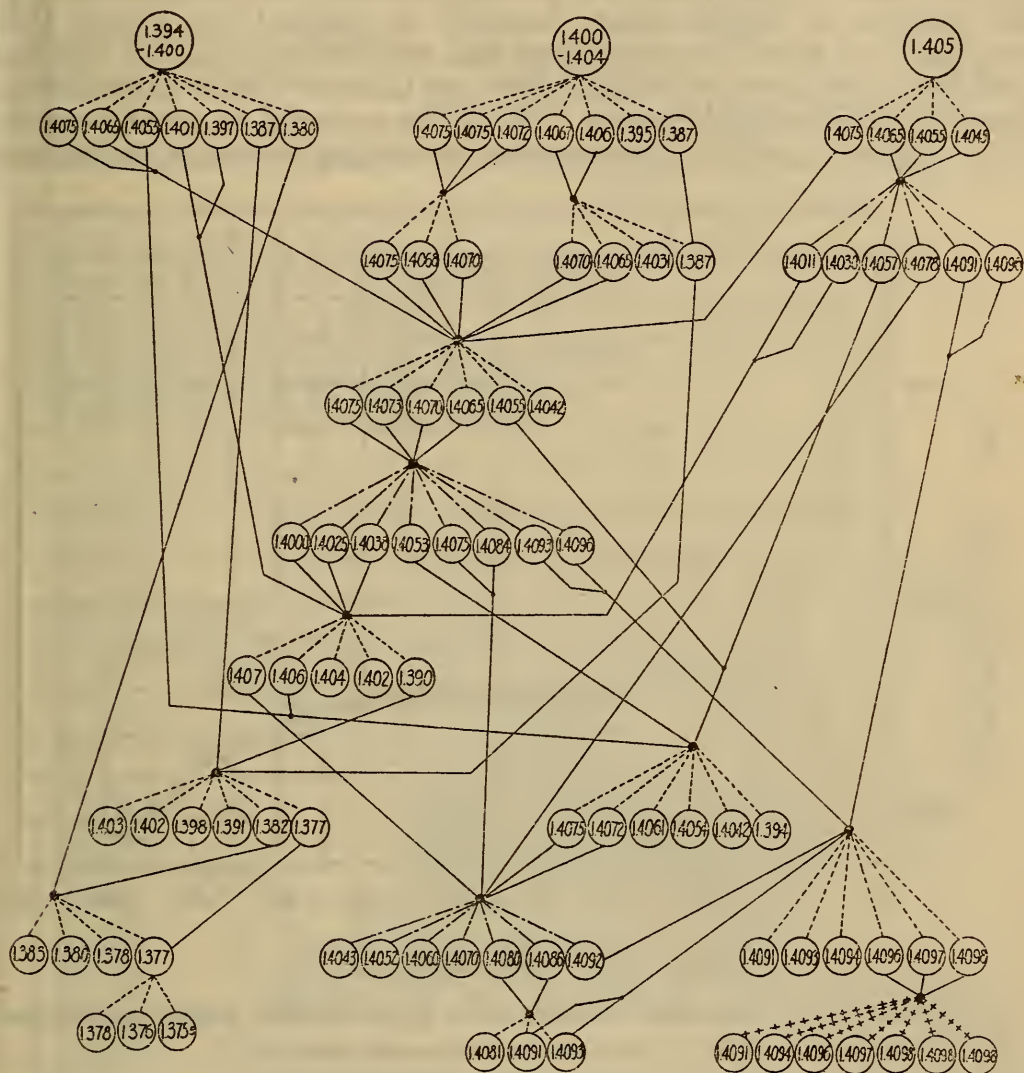
- - - - - - - MIXTURE FRACTIONATED BY EQUILIBRIUM MELTING

—◁— FRACTIONS MIXED

— — DISTILLATION WITH METHYL ALCOHOL

· · · · · · · DISTILLATION IN MICRO STILL

(401) FRACTION (Numbers indicate refractive index.)

1. A eutectic mixture freezing at −143.5° C. This mixture consisted presumably of *n*-hexane and methylcyclopentane. (See below.)

2. A small *n*-hexane fraction with refractive index 1.3755. Further work on this fraction was dispensed with because the separation of *n*-hexane had been previously accomplished (14).

3. A fraction freezing at $-141.9°$ C. The physical constants of this fraction were determined and were found to agree with those of pure synthetic methylcyclopentane. (See Table 1.) It should be noted, however, that the values for the refractive index, specific gravity, and boiling point are of comparatively little significance for the purpose of identification, because, as pointed out above, these constants for methylcyclopentane and ethylcyclobutane are identical within the accuracy with which they are known. Under these circumstances the freezing behavior (15) of the material is usually conclusive. Figure 5 gives a time-temperature cooling curve for the isolated
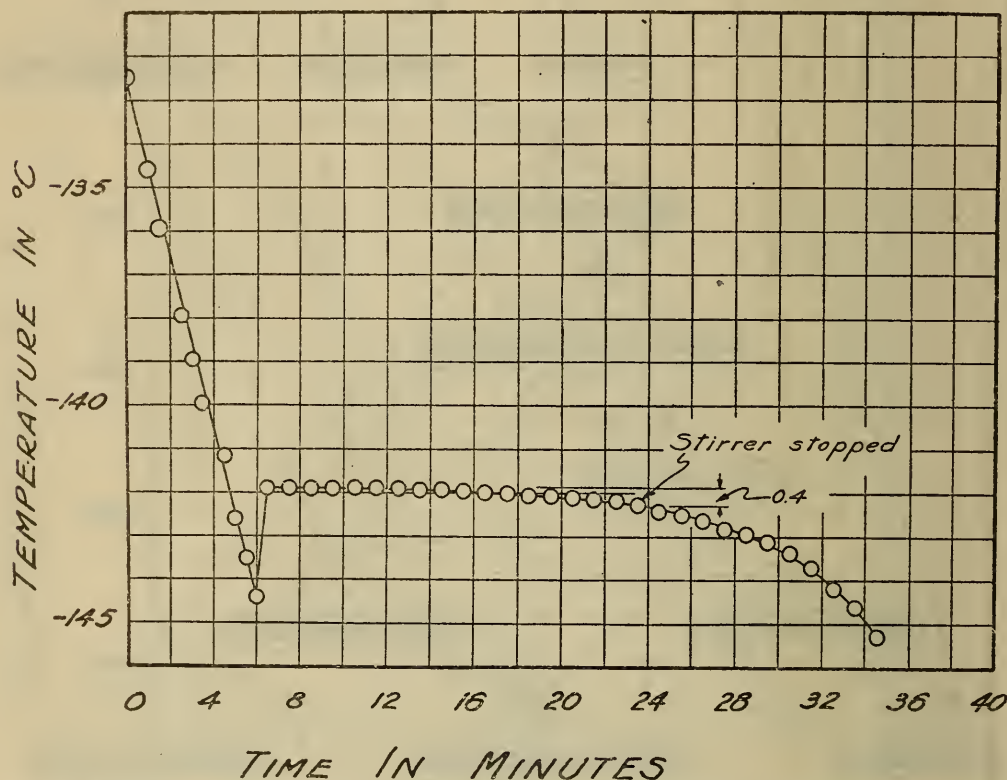

FIGURE 5.—*Time-temperature cooling curve of the isolated methylcyclopentane*
Initial freezing point: −141.9° C. The whole sample froze solid within 0.4° C.

sample. Half of it froze solid within about 0.2°. The initial freezing point $-141.9°$ C., must therefore be lower than that of the pure hydrocarbon by about 0.4° (16). The freezing point of the latter is therefore about $-141.5°$ C., which agrees substantially with the value $-141.0° \pm 0.3°$ C. reported by Timmermans. (See Table 1.) Unfortunately, the freezing point of ethylcyclobutane is not on record, so that the above evidence for identification is not wholly conclusive. Since, however, it is extremely unlikely that both the freezing point of ethylcyclobutane and its critical temperature of solution in aniline are identical with the corresponding values for methylcyclopentane, the identification may be assumed to be substantially established.

TABLE 1.—*Physical constants of methylcyclopentane and ethylcyclobutane*

|	Molecular weight	Boiling point	Freezing point	d_D^{20}	n_D^{20}	C. T. S. aniline
		°C.	°C.			°C.
Methylcyclopentane (from petroleum)____	[1] 84.1 ±0.2	71.8	−141.9	[2] 0.7487	1.4098	[3] 34.7
Synthetic methylcyclopentane_____	84.092	[4] 72—72.2	_____	[4] .7483	[4] 1.4088	_____
	_____	[5] 72	_____			[5] 35
	_____	[6] 71.9	[7] −141.0 ±0.3	[6] .7482	[6] 1.4103	[6] 34.7
Synthetic ethylcyclobutane_____	84.092	[8] 72.2 72.5	_____	[8] .745	[8] 1.4082	_____
	_____	[9] 70.6	_____	[9] .7284	[9] 1.404	_____

[1] Method described by M. M. Hicks-Bruun, B. S. Jour. Research, vol. 5, pp. 575–83, 1930.
[2] Determined by B. S. Section of Capacity and Density.
[3] For method see J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 7, p. 612, 1931.
[4] N. Zelinsky, Ber., vol. 44, p. 2781, 1911.
[5] G. Chavanne and L. J. Simon, Compt. rend., vol. 168, pp. 1112 and 1326, 1919.
[6] G. Chavanne, Bull. Soc. Chim. Belg., vol. 31, p. 338, 1922.
[7] Determined by J. Timmermans, see reference 5.
[8] N. Zelinsky and J. Gutt, Ber., vol. 41, p. 2432, 1908.
[9] J. Kishner, Chem. Zentr., vol. 34II, p. 2132, 1913.
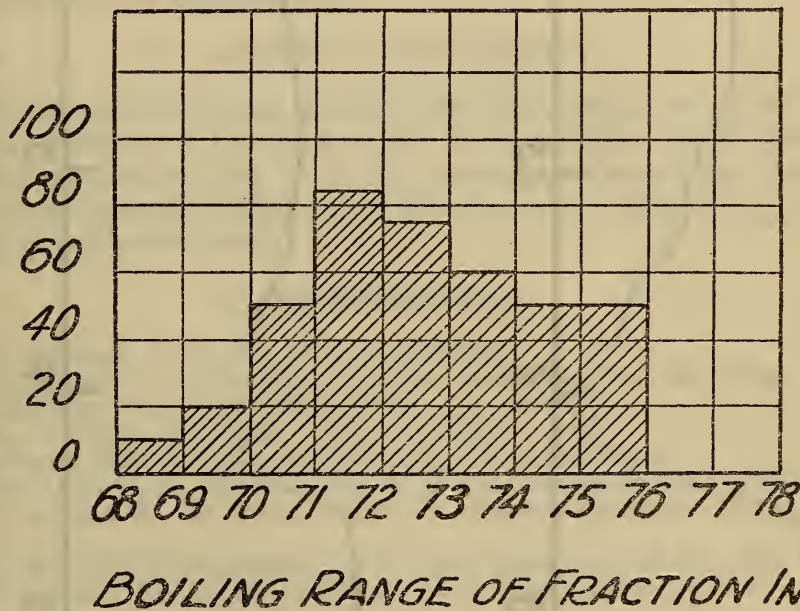
FIGURE 6.—*Amount of methylcyclopentane found in the petroleum*

Ordinate: Weight per cent of methylcyclopentane in the petroleum fraction
Abscissa: Boiling range of fraction in ° C.

On this assumption the purity of the hydrocarbon can be calculated by comparing its initial freezing point with that of pure methylcyclopentane and computing the amount of impurity required to produce the corresponding freezing-point depression. To make this calculation, the heat of fusion of methylcyclopentane is required. Since no value for this quantity is on record, an approximate and sufficiently accurate value was computed with the aid of the observed eutectic temperature of the system in the following manner (17): Since the eutectic liquid is saturated also with *n*-hexane, the melting point and latent heat of fusion of which are known, the eutectic composition was first calculated and found to be 95.9 mole per cent of methylcyclopentane. From this composition and the difference between the eutectic temperature and the freezing point of pure methylcyclopentane the value
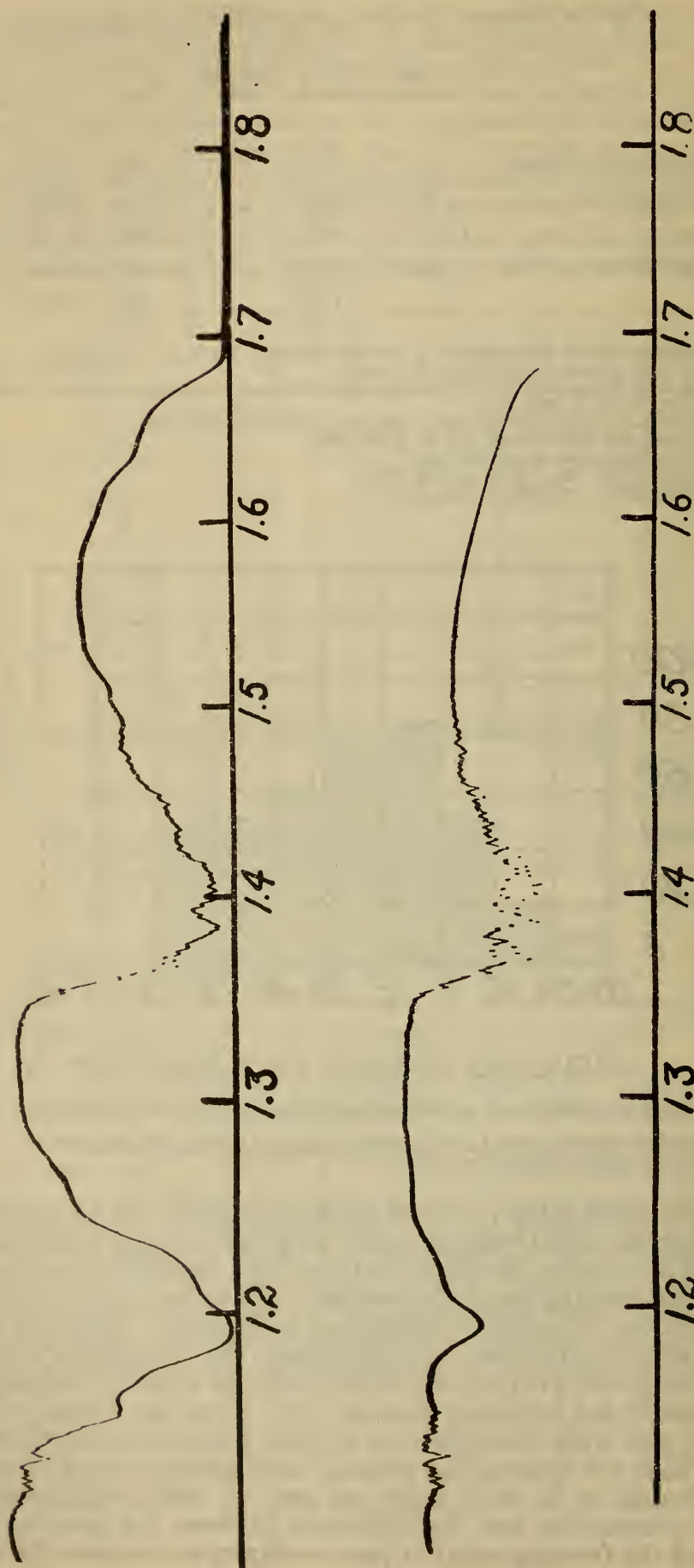
FIGURE 7.—*The infra-red absorption spectrum of the isolated methylcyclopentane*

These curves are the energy transmission lines of emission from a tungsten filament lamp through 1 cm. and 1 mm. cells, respectively. The bands at 1.71 μ and 1.2 μ are the second and third harmonies, respectively, of the fundamental at 3.4 μ attributed to the hydrogen-to-carbon vibration. The effective slit width is about 10 A. Measured by U. Liddel, of the Fixed Nitrogen Laboratory, U. S. Department of Agriculture

7.6 calories per gram was calculated for the latent heat of fusion of methylcyclopentane. Using this value, the composition of the various methylcyclopentane fractions shown by points 2 to 3 on the diagram of Figure 3 were then calculated, as was also the composition of the best sample of methylcyclopentane isolated from the petroleum. For these calculations Timmerman's value $-141.0 \pm 0.3°$ C. was used as the freezing point of pure methylcyclopentane and the calculation gave 98.9 ± 0.2 mole per cent as the purity of the methylcyclopentane isolated from petroleum.

Figure 6 shows the weight per cent of methylcyclopentane in the petroleum fractions boiling from 68° to 78° C. From Figures 2 and 6 the amount of methylcyclopentane present in these fractions is calculated. Their distribution and mass in grams (total about 4.5 kg) are shown by the black portion of the chart in Figure 2. This is equivalent to about one-fifth of 1 per cent of the crude petroleum used and is considered to be a conservative estimate of the amount of methylcyclopentane present.

Figure 7 shows the infra-red absorption spectrum of the liquid. This work was done by U. Liddel, of the Fixed Nitrogen Research Laboratory, Department of Agriculture.

IV. ACKNOWLEDGMENT

V. REFERENCES

1. W. Markownikoff, Ann., vol. 307, p. 343, 1899.
2. C. F. Mabery and O. J. Sieplein, Proc. Am. Acad. Sci., vol. 36, p. 285, 1901.
3. O. Aschan, Ber., vol. 31, p. 1803, 1898.
4. S. Young, J. Chem. Soc., vol. 73, p. 913, 1898.
5. G. Chavanne, Bull. Soc. Chem. Belg., vol. 31, p. 300, 1911.
6. J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 7, p. 607, 1931.
7. J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 6, p. 872, 1931.
8. R. T. Leslie and S. T. Schicktanz, B. S. Jour. Research, vol. 6, p. 377, 1931.
9. J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 5, p. 934, 1930.
10. E. W. Washburn, J. H. Bruun, and M. M. Hicks, B. S. Jour. Research, vol. 2, p. 469, Table 1, 1929.
11. N. Zelinsky and J. Gutt, Ber., vol. 41, p. 2432, 1908.
12. J. Kishner, Chem. Zentr., vol. 34II, p. 2132, 1913.
13. J. H. Bruun and S. T. Schicktanz, B. S. Jour. Research, vol. 7, pp. 851–882, 1931.
14. J. H. Bruun and M. M. Hicks-Bruun, B. S. Jour. Research, vol. 6, pp. 869–79, 1931.
15. E. W. Washburn, Ind. Eng. Chem., vol. 22, p. 985, 1930.
16. W. P. White, J. Phys. Chem., vol. 24, p. 393, 1920.
17. For the evidence justifying this procedure, see Washburn, Principles of Physical Chemistry, 2d ed., McGraw-Hill Book Co., New York, 1921, p. 206.

Note—While the manuscript of this paper was in the hands of the printer an account of a direct experimental determination of the latent heat of fusion of methylcyclopentane appeared by H. M. Huffman, G. S. Parks and M. Barmore, J. Am. Chem. Soc., vol. 53, p. 3882; 1931.

If this experimental value, 19.5 calories per gram, is used in place of our computed value, the purity of our methylcyclopentane is calculated to be 97.2 per cent.

WASHINGTON, July 24, 1931.